

Long-time dynamics of Rouse-Zimm polymers in dilute solutions with hydrodynamic memory

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The dynamics of flexible polymers in dilute solutions is studied taking into account the hydrodynamic memory, as a consequence of fluid inertia. As distinct from the Rouse-Zimm (RZ) theory, the Boussinesq friction force acts on the monomers (beads) instead of the Stokes force, and the motion of the solvent is governed by the nonstationary Navier-Stokes equations. The obtained generalized RZ equation is solved approximately. It is shown that the time correlation functions describing the polymer motion essentially differ from those in the RZ model. The mean-square displacement (MSD) of the polymer coil is at short times $\sim t^2$ (instead of $\sim t$). At long times the MSD contains additional (to the Einstein term) contributions, the leading of which is $\sim \sqrt{t}$. The relaxation of the internal normal modes of the polymer differs from the traditional exponential decay. It is displayed in the long-time tails of their correlation functions, the longest-lived being $\sim t^{-3/2}$ in the Rouse limit and $t^{-5/2}$ in the Zimm case, when the hydrodynamic interaction is strong. It is discussed that the found peculiarities, in particular an effectively slower diffusion of the polymer coil, should be observable in dynamic scattering experiments.

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I. INTRODUCTION

Most of the theoretical investigations on the dynamic properties of flexible macromolecules performed so far are based on the Rouse-Zimm (RZ) model [1, 2, 3, 4]. In this theory the polymer molecule is modeled as a chain of beads under Brownian motion. The bead participates in the interactions with solvent molecules. The solvent contributes a frictional force against the motion of a monomer and a random force to take into account the random collisions exerted on monomers. In the Rouse model, the solvent is considered nonmoving. Within the Zimm theory, the motion of each monomer also affects other monomers, via the flow which it induces in the ambient medium. It has been shown that the Zimm model predicts the correct dynamical behavior for dilute polymer solutions in θ -conditions. The Rouse model is applicable for good solvents, where the corrections due to the hydrodynamic interactions and excluded volume effects cancel each other to a large extent, or in the situations when the surrounding polymers screen out the hydrodynamic interactions [3, 4]. Both models assume Gaussian equilibrium distribution of the beads, which is in most cases the only description of a polymer that can be manipulated analytically. The models hold for such polymer properties, which involve length scales that are large compared to monomer sizes. Although the RZ model is considered a universal theory well describing the long-time behavior of the polymer macromolecules, there is still a number of unresolved problems in the understanding of the polymer dynamics in solution [5, 6]. So, the q^3 dependence of the first cumulant in the intermediate scattering vector regime is well confirmed for synthetic

polymers and DNA, however, the experimental values are smaller than the theoretical predictions. Systematic deviations from the theoretical behavior at large scattering vectors q have been found for various polymers using quasi-elastic neutron scattering. At small q the diffusion coefficient calculated from the continuous RZ model also deviates from the experimental values for both the natural and synthetic macromolecules. For a review of these and other difficulties of the RZ theory we refer also to the earlier work [7]; it can be seen that the situation has changed little during a decade.

In this work we propose a generalization of the RZ theory that could provide a better understanding of the dynamical behavior of polymers in dilute solutions. The bead and fluid inertia during the motion of the polymer in the solvent have been taken into account. Also the hydrodynamic interaction is considered by solving the nonstationary Navier-Stokes equations. A possible importance of such a development (in connection with the Rouse model) was already discussed in Ref. 8. As distinct from the traditional approach to the polymer dynamics [1, 2, 3, 4], in our theory the resistance force on the moving bead will not be assumed the Stokes one, which is proportional to the velocity of the bead. We model this force by the Boussinesq-Basset history force [9, 10, 11] which, at a given time t , is determined by the state of the bead motion in all the preceding moments of time. We thus have a possibility to obtain solutions valid for almost arbitrary t (for incompressible fluids, however, $t >> b/c$, where b is the monomer size and c the sound velocity). The discussed generalization means that the effects of hydrodynamic memory are taken into account. Such effects are extensively studied in the physics of sim-

ple liquids and in the theory of Brownian motion (see e.g. Ref. [12]) with very important consequences. In particular, the memory effects are revealed in such interesting peculiarities like the famous "long-time tails" of the molecular velocity autocorrelation function (VAF), first discovered by means of computer experiments [13, 14]. The concept of the Brownian motion lies in the basis of the RZ theory of polymer dynamics. Thus it is natural to expect that the memory effects are important to polymers as well. An attempt to show it was done in our recent paper [15] where the Rouse model has been considered taking into account the hydrodynamic memory but with no hydrodynamic interaction. Here we present a more general theory that, as limiting cases, includes both the Rouse and Zimm models. It will be shown that the inclusion of the hydrodynamic memory into the classical RZ model leads to an essentially different behavior of the time correlation functions describing the polymer motion in solution. It will be demonstrated by the appearance of long-time tails of these functions that reflect a strong persistence of the correlation with the initial state of the polymer. The relaxation of the mean square displacement of the whole polymer, as well as the decay of the polymer internal modes, are slower than in the original model. We also show how the tails are displayed in the long-time behavior of the Van Hove function used in the interpretation of quasi-elastic scattering of light and neutrons. It is discussed that the found new features in the polymer dynamics should be observable in the scattering experiments. Moreover, we believe that the obtained results could contribute to the solution of some of the existing problems between the theory and experiment.

II. THE DYNAMICS OF POLYMERS WITH HYDRODYNAMIC MEMORY

Within the RZ model the motion of the n th polymer segment (the bead) of a flexible polymer coil consisting of N beads is described by the equation

$$M \frac{d^2 \vec{x}_n(t)}{dt^2} = \vec{f}_n^{\text{fr}} + \vec{f}_n^{\text{ch}} + \vec{f}_n. \quad (1)$$

Here, \vec{x} is the position vector of the bead, M is its mass, \vec{f}_n^{ch} is the force from the neighboring beads along the chain, \vec{f}_n is the random force due to the motion of the molecules of solvent, and \vec{f}_n^{fr} is the friction force on the bead during its motion in the solvent. In the RZ model the latter force was

$$\vec{f}_n^{\text{fr}} = -\xi \left[\frac{d\vec{x}_n}{dt} - \vec{v}(\vec{x}_n) \right], \quad (2)$$

with $\vec{v}(\vec{x}_n)$ being the velocity of the fluid in the place of the n th bead due to the motion of other beads. The friction coefficient for a spherical particle of radius b is $\xi = 6\pi\eta b$, where η is the solvent viscosity. However,

this expression holds only for the steady-state flow. In the general case the resistance on the body moving in a liquid depends on the whole history of the motion, i.e. on velocities and accelerations in the preceding moments of time. For incompressible fluids we use the Boussinesq force [9, 16] instead of Eq. (2). This means that we replace, in the Fourier transformation (FT) with respect to the time, the friction coefficient ξ with the frequency dependent quantity

$$\xi^\omega = \xi \left[1 + \chi b + \frac{1}{9} (\chi b)^2 \right], \quad (3)$$

where $\chi = \sqrt{-i\omega\rho/\eta}$, ($\text{Re}\chi > 0$) and ρ is the density of the solvent. The Boussinesq force follows naturally from the usual hydrodynamics as the solution of linearized Navier-Stokes equations [17, 18]. Additionally to the Stokes force it contains terms which, if the fluid density is comparable to the density of the bead, cannot be neglected for the nonstationary motion when they are of the same order as the inertial term in Eq. (1). Equations (1-3) have to be solved together with the hydrodynamic equations for the velocity of the solvent,

$$\rho \frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta \Delta \vec{v} + \vec{\varphi}, \quad \nabla \cdot \vec{v} = 0. \quad (4)$$

Here p is the pressure. The quantity $\vec{\varphi}$ is an external force per unit volume [4],

$$\vec{\varphi}(\vec{x}) = - \sum_n \vec{f}_n^{\text{fr}}(\vec{x}_n) \delta(\vec{x} - \vec{x}_n). \quad (5)$$

Equations (4) are solved using the FT in coordinates and time. The solution can be, for any of the components $\alpha = x, y$, or z written in the form

$$v_\alpha^\omega(\vec{r}) = \int d\vec{r}' \sum_\beta H_{\alpha\beta}^\omega(\vec{r} - \vec{r}') \varphi_\beta^\omega(\vec{r}'), \quad (6)$$

with the FT of the Oseen tensor

$$H_{\alpha\beta}^\omega(\vec{r}) = A \delta_{\alpha\beta} + B r_\alpha r_\beta r^{-2}, \quad (7)$$

$$A = (8\pi\eta r)^{-1} \{ e^{-y} - y [(1 - e^{-y}) y^{-1}]'' \},$$

$$B = (8\pi\eta r)^{-1} \{ e^{-y} + 3y [(1 - e^{-y}) y^{-1}]'' \}. \quad (8)$$

Here the prime denotes the differentiation with respect to $y = r\chi$. Substituting φ_β^ω from the FT of Eq. (5) to v_α^ω from (6), and the obtained result into the FT of equation of motion (1), we get a generalization of the RZ equation, which in the continuum approximation reads

$$-i\omega x_{n\alpha}^\omega = \frac{1}{\xi^\omega} [f_{\alpha}^{\text{ch},\omega}(n) + f_\alpha^\omega(n) + M\omega^2 x_\alpha^\omega(n)] \quad (9)$$

$$+ \int_0^N dm H_{\alpha\beta nm}^\omega \left[\frac{3k_B T}{a^2} \frac{\partial^2 x_\beta^\omega}{\partial m^2} + f_\beta^\omega(m) + M\omega^2 x_\beta^\omega(m) \right]$$

where a is the mean square distance between neighboring beads along the chain. It has been used that the force between the beads can be obtained from the effective potential $u = (3k_B T/2a^2) \sum_{n=2}^N (\vec{x}_n - \vec{x}_{n-1})^2$ which follows from the equilibrium (Gaussian) distribution of the beads [3, 4]. Due to the dependence of the Oseen tensor on the difference $\vec{r}_{nm} = \vec{x}(n) - \vec{x}(m)$, Eq. (9) is nonlinear and thus hardly solvable analytically. We use the common approximation of preaveraging of the tensor over the equilibrium distribution $P(r_{nm}) = (2\pi a^2 |n - m|/3)^{-3/2} \exp[-3r_{nm}^2/(2a^2 |n - m|)]$:

$$\langle H_{\alpha\beta nm}^\omega \rangle_0 = \delta_{\alpha\beta} h^\omega(n - m), \quad (10)$$

$$h^\omega(n - m) = \frac{1}{\sqrt{6\pi^3 |n - m| \eta a}} \left[1 - \sqrt{\pi} z e^{z^2} \operatorname{erfc}(z) \right],$$

with $z \equiv \chi a (|n - m|/6)^{1/2}$. In the case without memory [4] the function h at large $|n - m|$ behaves as $\sim |n - m|^{-1/2}$; now the effective interaction between the beads disappears more rapidly, $\sim |n - m|^{-3/2}$. Since Eq. (9) now contains only the diagonal terms, it can be solved using the FT in the variable n , $\vec{x}^\omega(n) = \vec{y}_0^\omega + 2 \sum_{p \geq 1} \vec{y}_p^\omega \cos(\pi np/N)$, where the boundary conditions at the ends of the chain have been taken into account [4], $\partial \vec{x}^\omega / \partial n = 0$ at $n = 0, N$. The inverse FT then yields the following equation for the Fourier components \vec{y}_p^ω :

$$\vec{y}_p^\omega = \vec{f}_p^\omega \left[-i\omega \Xi_p^\omega - M\omega^2 + K_p \right]^{-1}, \quad (11)$$

where $\Xi_p^\omega \equiv \xi^\omega [1 + (2 - \delta_{p0}) N h_{pp}^\omega]^{-1}$, and $K_p \equiv 3\pi^2 p^2 k_B T / (Na)^2$, $p = 0, 1, 2, \dots$. The matrix h_{pp}^ω is defined by the integral

$$h_{pp}^\omega = \frac{1}{N^2} \int_0^N dn \int_0^N dm h^\omega(n - m) \cos \frac{\pi p n}{N} \cos \frac{\pi p m}{N}. \quad (12)$$

In obtaining Eq. (11) the fact that the nondiagonal elements of the matrix are small in comparison with the diagonal ones and can be in the first approximation neglected has been already taken into account; the substantiation of this is the same as in Refs. [3,4]. Equation (11) can be investigated as it is usually done in the theory of Brownian motion. One can use the fluctuation-dissipation theorem (FDT) [18] or the properties of the random forces [12]. The forces acting on different beads n and m are uncorrelated, thus their correlator is $\sim \delta_{nm}$. In going to the continuum approximation the Kronecker symbol has to be replaced by the δ -function, $\delta(n - m)$, so in the FT we have

$$\langle f_{p\alpha}^\omega f_{q\alpha}^{\omega'} \rangle = \frac{k_B T \operatorname{Re} \Xi_p^\omega}{(2 - \delta_{p0}) \pi N} \delta_{\alpha\beta} \delta_{pq} \delta(\omega + \omega'). \quad (13)$$

Equation (11) then yields the following expression for the time correlation function of the Fourier components $y_{\alpha p}$,

$$\psi_p(t) = \langle y_{\alpha p}(0) y_{\alpha p}(t) \rangle:$$

$$\psi_p(t) = \frac{k_B T}{(2 - \delta_{p0}) \pi N} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t} \operatorname{Re} \Xi_p^\omega}{| -i\omega \Xi_p^\omega - M\omega^2 + K_p |^2}, \quad (14)$$

in agreement with the FDT. The generalized susceptibility is $\alpha_p(\omega) = [(2 - \delta_{p0}) N]^{-1} [-i\omega \Xi_p^\omega - M\omega^2 + K_p]^{-1}$, and the generalized forces corresponding to the coordinates $y_{\alpha p}^\omega$ are $N f_{p\alpha}^\omega$. Using the Kramers-Kronig relation [19], the same initial value for the function ψ_p at $t = 0$ as in the RZ theory is obtained: $\psi_p(0) = k_B T \alpha_p(0) = k_B T (2N K_p)^{-1}$, $p > 0$.

Equation (14) gives the solution of the model. Knowing $\psi_p(t)$, other correlation functions of interest can be found, e.g. the VAF, $\Phi_p(t) = \langle v_{\alpha p}(0) v_{\alpha p}(t) \rangle = -d^2 \psi_p(t) / dt^2$, or the mean square displacement (MSD), $\langle \Delta y_p^2(t) \rangle = 2[\psi_p(0) - \psi_p(t)]$. The previous RZ results in the absence of memory are obtained by putting $\omega = 0$ in Ξ_p^ω , Eq. (11), and $M = 0$. The mode y_0 describes the motion of the center of inertia of the coil [3, 4]. In the RZ case we get $\psi_0(0) - \psi_0(t) = D_C t$. The diffusion coefficient $D_C = k_B T (h_{00}^0 + 1/N\xi)$ contains the Zimm ($D_C = 8k_B T (3\sqrt{6\pi^3 N \eta a})^{-1}$) and Rouse ($D_C = k_B T / N\xi$) limits. The internal modes ($p > 0$) relaxed exponentially, $\psi_p(t) = (k_B T / 2N K_p) \exp(-t/\tau_p)$, with the relaxation times $\tau_p = \xi / [K_p (1 + 2N h_{pp}^0 \xi)]$, where $h_{pp}^0 = (12\pi^3 N p)^{-1/2} (\eta a)^{-1}$.

A. The Rouse limit with memory

Now let us consider the case with memory, the limit of Rouse [15]. It assumes that the hydrodynamic interaction contribution to Ξ_p^ω in Eq. (11) is negligible for all ω s. The subsequent equations then change only by the substitution $\Xi_p^\omega \approx \xi^\omega$. The corresponding integral in Eq. (14) is encountered in the theory of Brownian motion of one particle: in the case when $p = 0$, the particle is free, and if $p > 0$, it is in a harmonic field with the force constant K_p . Such problems were solved in a number of investigations beginning from the work [16]. Adopting the known solutions, see e.g. Ref. [12], for the MSD of the coil we have the following asymptotic expression:

$$\langle \Delta y_0^2(t) \rangle = 2D_C t \left[1 - \frac{2}{\sqrt{\pi}} \sqrt{\frac{\tau_b}{t}} + \frac{2}{9} \left(4 - \frac{M}{M_s} \right) \frac{\tau_b}{t} - \dots \right], \quad (15)$$

where $t \gg \tau_b = b^2 \rho / \eta$ and M_s is the mass of the solvent displaced by one bead. For small times $\langle \Delta y_0^2(t) \rangle \approx k_B T t^2 / N (M + M_s/2)$. (The physically correct value $k_B T t^2 / N M$ can be obtained only if the compressibility is taken into account [12, 16].) It is well seen from Eq. (15) and confirmed by numerical calculations of Eq. (14) how slowly the previous result is approached: the second (\sqrt{t}) term is less than 1 per cent of the first only for $t > 10^4 \tau_b$. For long chains when the terms $\sim M$ can be neglected, at $t = 10\tau_b$ the MSD constitutes only about 3/4 of the

Einstein limit. Note that for the motion of the coil as a whole the exact analytical solution exists which differs from the known solution for one Brownian particle only by a factor $1/N$ [16, 20]. For example, the VAF of the center of mass of the Rouse coil is

$$\Phi_0(t) = \frac{\Phi_0(0)}{\lambda_1 - \lambda_2} \sum_{i=1,2} (-1)^{i+1} \lambda_i e^{(\lambda_i^2 t)} \operatorname{erfc}(\lambda_i \sqrt{t}), \quad (16)$$

where $\Phi_0(0) = k_B T / (M + M_s/2)N$ and λ_i are the (complex) roots of the equation $\lambda^2 + \sqrt{\tau_b} \lambda / \tau + 1/\tau = 0$ with $\tau = (M + M_s/2)/\xi$.

The long-time asymptote of the function $\psi_{p>0}(t)$ describing the relaxation of the Rouse modes is

$$\frac{\psi_p(t)}{\psi_p(0)} = -\frac{1}{2\sqrt{\pi}} \frac{\tau_p}{\tau_b} \left[\left(\frac{\tau_b}{t} \right)^{3/2} + 3 \frac{\tau_p}{\tau_b} \left(\frac{\tau_b}{t} \right)^{5/2} + \dots \right]. \quad (17)$$

B. The Zimm case

For the Zimm model, when the hydrodynamic interaction is strong for all frequencies that significantly contribute to the studied correlation functions, we have in Eq. (11) $\Xi_p^\omega \approx [(2 - \delta_{p0}) N h_{pp}^\omega]^{-1}$. The Oseen matrix (12) can be calculated with any degree of precision, e.g. for $p = 0$ we have the exact result

$$h_{00}^\omega = \frac{3\sqrt{\pi}}{4\tilde{z}} h_{00}^0 \left[1 - \frac{2}{\sqrt{\pi}\tilde{z}} - \frac{1}{\tilde{z}} \left(e^{\tilde{z}^2} \operatorname{erfc}\tilde{z} - 1 \right) \right], \quad (18)$$

where $\tilde{z} \equiv (N\chi a/6)^{1/2}$. Then in the t -representation the correlation function can be obtained using the standard methods [12]. Here we show the main terms of the asymptotic expansion of the time correlation functions that can be found also by using the expansion of the susceptibility $\alpha_p(\omega)$ in small $(-i\omega)^{1/2}$. In the case of the diffusion of the coil as a whole we obtain the expression similar to Eq. (15),

$$\psi_0(0) - \psi_0(t) = D_C \left[t - \frac{2}{\sqrt{\pi}} (\tau_R t)^{1/2} + \dots \right]. \quad (19)$$

The characteristic time in this equation is $\tau_R = R^2 \rho / \eta$. The form of Eq. (19) exactly corresponds to that familiar in the theory of Brownian motion of rigid particles of radius R . Here R is the hydrodynamic radius of the coil [3, 4], determined from the relation $D_C = k_B T / (6\pi R \eta)$ where D_C is the Zimm diffusion coefficient. In the standard model of Gaussian chains the radius R is given also by the Kirkwood relation [3] $R^{-1} = N^{-2} \sum_{n=1}^N \sum_{m=1, m \neq n}^N \langle r_{nm}^{-1} \rangle \approx 8\sqrt{2/3\pi N}/a$, where r_{nm} is the distance between the beads and $N >> 1$.

Consider now the internal modes of the polymer, $p > 0$. The components of the matrix (12) are calculated as in Ref. [4] and can be expressed through special functions, so that their expansion is known to any desired power

of $\sqrt{-i\omega}$. The first correction to the classical result is determined by the coefficient at the term $(-i\omega)$. The first nonvanishing correction to the susceptibility $\alpha_p(\omega)$ is given by the term $(-i\omega)^{5/2}$. The coefficient at this term is determined by the expansion coefficients at the terms $(-i\omega)$ and $(-i\omega)^{3/2}$ in the expansion of h_{pp}^ω . For the correlation function $\psi_{p>0}(t)$, using Eq. (14), we thus find

$$\frac{\psi_p(t)}{\psi_p(0)} \approx -\frac{2^9}{45\pi^3} \sqrt{\frac{2}{\pi}} \left(1 + \frac{16}{3\pi^2 p} \frac{\tau_R}{\tau_p} \right) \frac{1}{p^3} \frac{\tau_p \tau_R^{3/2}}{t^{5/2}}, \quad (20)$$

where $t >> \tau_R$ and $\tau_p = (Na^2)^{3/2} (\eta/k_B T) (3\pi p^3)^{-1/2}$ is the Zimm relaxation time [3, 4].

C. End-to-end vector and the dynamic structure factor

Having the solutions (17) and (20), the evolution of the end-to-end vector of the chain can be investigated. From the relation $\vec{R}(t) = \vec{x}(t, N) - \vec{x}(t, 0) = -4 \sum_{p=1,3,\dots} \vec{y}_p(t)$ one finds

$$\Phi(t) = \langle \vec{R}(t) \vec{R}(0) \rangle = 48 \psi_1(0) \sum_{p=1,3,\dots} \frac{1}{p^2} \frac{\psi_p(t)}{\psi_p(0)} \quad (21)$$

for both the models. For the Rouse model at long times

$$\Phi(t) = -\frac{\pi^4}{4\sqrt{\pi}} \frac{\tau_1 \tau_b^{1/2}}{t^{3/2}} \psi_1(0) \left(1 + \frac{3\pi^2}{10} \frac{\tau_1}{t} + \dots \right), \quad (22)$$

and in the Zimm case the long-time asymptote reads

$$\Phi(t) \approx -3\sqrt{2\pi} \psi_1(0) (\tau_R + 1.85\tau_1) \tau_R^{3/2} t^{-5/2}. \quad (23)$$

(In Eqs. (22) and (23) $\tau_{p=1}$ is the relaxation time for the corresponding model.)

Finally, we give the result for the intermediate scattering function $G(\vec{k} t) = N^{-1} \sum_{nm} \langle \exp\{i \vec{k} [\vec{x}_n(t) - \vec{x}_m(0)]\} \rangle$ that is used in the description of the dynamic light or neutron scattering from a polymer coil [3] (\vec{k} is the wave-vector change at the scattering). Acting in a similar way as in Ref. [3], $G(\vec{k}, t)$ can be for large t approximated by the expression

$$G(k, t) \approx N \exp \left\{ -k^2 [\psi_0(0) - \psi_0(t)] \right\} \times \exp \left[\frac{-Na^2 k^2}{36} \left(1 - \frac{8N^2 a^4 k^4}{3\pi^6} \sum_{p=2,4,\dots}^{\infty} \frac{1}{p^6} \frac{\psi_p(t)}{\psi_p(0)} \right) \right] \quad (24)$$

valid for $kR \ll 1$ (in the opposite case, the function $G(k, t)$ becomes very small at long times). Equation (24) is equally applicable for both considered models, if the corresponding Eqs. (15) and (17) for the Rouse case, or (19) and (20) for the Zimm model are substituted here. One can see that the contribution of the internal modes is small and thus hardly detectable against the diffusion

term given by the first exponential. However, our predictions concerning the diffusion of the coil as a whole,

$$G(k, t) \approx N \exp \{ -k^2 [\psi_0(0) - \psi_0(t)] \}, \quad (25)$$

could be directly measured in the scattering experiments.

III. CONCLUSION

We conclude that in the generalized RZ model, when the memory of the viscous solvent is taken into account, the relaxation of the correlation functions describing the polymer motion essentially differs from the original theory. The MSD is at short times $\sim t^2$ (instead of $\sim t$). At long times it contains additional (to the Einstein term) contributions, the leading of which is $\sim \sqrt{t}$. The internal normal modes of the polymer motion now do not relax exponentially. It is well displayed in long-time tails of their time correlation functions. The longest-lived contribution to the correlation function of the bead displacement is $\sim t^{-3/2}$ in the Rouse limit and $t^{-5/2}$ in the Zimm case, when the hydrodynamic interaction is strong. It would be interesting to investigate the found peculiarities using computer simulation methods and experimentally, e.g. by the dynamic light or neutron scattering. Simple estimations show that the relaxation of the internal modes, $\psi_{p>0}(t)$, although qualitatively different from the previous RZ model, for real polymers only slightly differs from the traditional exponential law $\sim \exp(-t/\tau_p)$, except at high frequencies (it is because the relaxation time for the internal modes, τ_p , is much larger than the characteristic times τ_b and τ_R). However, the differences from the original model, at least for the Zimm case, should be experimentally accessible. Due to the long-range character of the hydrodynamic field, the characteristic time of the Zimm model, τ_R , is determined by the size of the whole coil. For a typical radius around 100 nm, the density and viscosity of water at room conditions, one gets τ_R about 10 nanoseconds ($\tau_R/\tau_{p=1} \approx 5 \times 10^{-4}$ sec). Taking into account the possibilities of current experiments (e.g. in Ref. [21] the dynamic structure factor of polymers in solution was studied using quasi-elastic light scattering in a time window beginning from 12.5 ns, and even shorter times are accessible by the neutron spin-echo technique [22]), and

the fact that the function $\psi_0(0) - \psi_0(t)$ approaches the Einstein limit $D_C t$ very slowly as t increases, the non-diffusive ("ballistic") motion of the polymer coil should be readily observable by the dynamic light and neutron scattering. In fact, similar experiments were successfully carried out on single Brownian particles. For example, using the diffusive wave spectroscopy the ballistic motion of polystyrene spheres with the radius $b = 0.206\mu\text{m}$ in aqueous solution (with the characteristic time τ_R about $0.04\mu\text{sec}$) was observed [23]. The size of such particles corresponds to the hydrodynamic radius of the DNA coil of a molecular weight $6 \times 10^6 \text{ g/mol}$ (with the diffusion coefficient $D_C \approx 1.3 \times 10^{-8} \text{ cm}^2/\text{s}$) [24]. The nondiffusive motion of even smaller (with a radius $< 100 \text{ nm}$) particles was observed in the experiments [25]. It has been found in these and other works that the apparent diffusion coefficient of Brownian particles is smaller than that following from the Einstein theory. These observations are very similar to the situation described by us for the polymer coils. The tails in the MSD lead to a slower decay of the dynamic structure factor (25). This corresponds to diffusion with an effectively smaller diffusion coefficient (as well as the first cumulant) than predicted by the previous theory. This is the long-standing unresolved "puzzle" between the theory and experiments. We believe that the proposed theory could help to solve this problem in the description of the dynamic scattering experiments on polymers [5, 6, 7] and thus to contribute to a deeper understanding of the dynamical properties of polymers.

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